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(54) Title: MANUFACTURE OF LITHOGRAPHIC PRINTING FORMS (57) Abstract Phenolic resin compositions formulated for use in lithographic exposure processes may be given a heat treatment at 40–90 °C for an extended period shortly after their coating onto lithographic substrates, to produce lithographic printing forms. It is found that such a heat treatment improves later exposure processes, in particular by rendering the sensitivity of the compositions less variable, over time.		

MANUFACTURE OF LITHOGRAPHIC PRINTING FORMS

5 The present specification relates to methods of manufacturing lithographic printing form precursors. The invention relates further to such lithographic printing form precursors per se, and to their use.

10 The art of lithographic printing is based on the immiscibility of ink, generally an oily formulation, and water, wherein in the traditional method the ink is preferentially retained by the image or pattern area and the water or fountain solution is preferentially retained
15 by the non-image or non-pattern area. When a suitably prepared surface is moistened with water and an ink is then applied, the background or non-image area retains the water whilst the image area accepts ink and repels the water. The ink on the image area is then transferred to
20 the surface of a material upon which the image is to be reproduced, such as paper, cloth and the like. Commonly the ink is transferred to an intermediate material called the blanket which in turn transfers the ink to the surface of the material upon which the image is to be reproduced.

25 New types of "waterless" lithographic printing employ only an oily ink material and preferentially ink-accepting image areas and ink-repelling non-image areas on the printing form.

30 A generally used type of lithographic printing form precursor (by which we mean a coated printing form prior to exposure and development) has a radiation sensitive coating applied to an aluminium substrate. Negative
35 working lithographic printing form precursors have a radiation sensitive coating which when imagewise exposed to radiation of a suitable wavelength hardens in the

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imaging technology is making new demands on coatings for lithographic printing.

5 It is known from GB 1245924 that the solubility of phenolic resins in lithographic developers may be increased by the application of heat. The heat may be delivered by infra-red radiation, assisted by radiation absorbing components such as carbon black or Milori Blue (C.I. Pigment Blue 27). However the developer resistance
10 of the non-exposed areas to commercial developers is low, and the solubility differential is low compared to the commercial UV sensitive compositions containing NQD moieties.

15 We have devised new positive working heat sensitive systems comprising phenolic resins, to meet the new demands. Our new systems and methods are the subject of our patent applications PCT/GB97/01117, GB 9700877.5 (taken forward as PCT/GB98/00132), GB 9714169.1 (taken
20 forward as PCT/GB98/01953, MY PI 9803095 and ZA 98/5913), GB 9714172.5 (taken forward as PCT/GB98/01957, MY PI 9803069 and ZA 98/5912), and GB 9722862.1, all unpublished at the priority date of this application. We have observed that in our new systems there may be an
25 alteration in their sensitivity over time, after the heat sensitive composition has been applied to a substrate and dried, such effect being the result of reduced developer solubility of the unexposed compositions with time prior to exposure. Thus when we mention "sensitivity" in this
30 specification we are considering this in the context of the entire process of exposure and development. We are not referring to the matter of how the areas of the composition which are exposed react to that exposure. Sometimes this "sensitivity" is called "operating speed"
35 in the art.

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preferably arranged to alter the developer solubility of the composition compared to when said modifying means is not present in a said composition. Said modifying means may be covalently bonded to said phenolic resin or may be
5 a compound which is not covalently bonded to said phenolic resin.

Said modifying means may be selected from:

10 - functional groups Q, as described in any statement hereinafter with regard to what is referred to as the "169 invention";

- diazide moieties;

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- nitrogen containing compounds wherein at least one nitrogen atom is either quaternized, incorporated in a heterocyclic ring or quaternized and incorporated in a heterocyclic ring, as described in any statement
20 hereinafter with regard to what is referred to as the "117 invention";

- latent Bronsted acids, onium salts or acid generating compounds as described in any statement
25 hereinafter with regard to further compositions.

Said heat sensitive composition preferably passes tests 1 to 5 described hereinafter with respect to the '117 invention wherein a reference in the tests to an
30 "active polymer" should be substituted with a reference to said phenolic resin, described above in the absence of said modifying means; and a reference to a "reversible insolubiliser compound" should be substituted with a reference to said modifying means.

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effective conditions, and the optimal conditions to achieve a substantially constant sensitivity over time, and at a practicable level, will vary from case to case, and can readily be determined by trial and error. We believe that a suitable heat treatment accelerates the formation of a stable network structure within the composition. If the elevated temperature is too low we believe the time required for this stable network structure to form is too long to be practicable. Furthermore in relation to the minimum suitable temperature it should be borne in mind that the elevated temperature should desirably not be less than that which the precursor might typically be subjected to in transit or in storage, or otherwise changes in sensitivity may occur. Consequently we favour carrying out the heat treatment at a temperature of at least 40°C, preferably at least 45°C, most preferably at least 50°C. As regards the upper limit, we believe that at too high a temperature the time for which the heat treatment should be carried out in order to obtain a desired level and stability of sensitivity is likely to be overly critical, and that even when the sensitivity is adequately stable, it is likely to be too low to be of use. Again, trial and error can easily be used to make this determination but as a guide we favour using a temperature not in excess of 90°C, preferably not in excess of 85°C, most preferably not in excess of 60°C.

We believe that temperatures in the range 50-60°C (inclusive) may be most favoured in the method of the present invention.

The time for the heat treatment can also be determined by trial and error. Generally, the lower the temperature for the heat treatment, the longer the time

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The solvent itself is not critical; any solvent in which the composition can be dissolved and which may be removed by evaporation after coating may be used.

5 It will be appreciated that a primary object of the invention is to render the sensitivity (as previously defined) of the composition less variable over time. This is suitably assessed over a period of time which is the longest interval likely, between the manufacture of the
10 printing form precursor and the use of the printing form precursor, by a customer. We regard one year as being a suitable period of time, for this assessment. In absolute terms, preferably the heat treatment is such that the sensitivity reduction in a given practical developer, for
15 example 14 wt% sodium metasilicate pentahydrate in water, of said composition over a one year period after the heat treatment does not exceed 15%; and preferably does not exceed 10%.

20 A further object of the present invention is that the sensitivity of the preferred compositions should be at a practicable level, after the heat treatment; but suitably no more than 400 mJcm², preferably no more than 250 mJcm², most preferably no more than 200 mJcm².

25 Novolak resins are useful in this invention, suitably being condensation reaction products between appropriate phenols, for example phenol itself, C-alkyl substituted phenols (including cresols, xylenols, p-tert-butyl-phenol,
30 p-phenylphenol and nonyl phenols), diphenols e.g. bisphenol-A (2,2-bis(4-hydroxyphenyl)propane), and appropriate aldehydes, for example formaldehyde, chloral, acetaldehyde and furfuraldehyde. The type of catalyst and
35 the molar ratio of the reactants used in the preparation of phenolic resins determines their molecular structure

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suitable for inclusion in the composition, in admixture with a phenolic resin, include: poly-4-hydroxystyrene; copolymers of 4-hydroxystyrene, for example with 3-methyl-4-hydroxystyrene or 4-methoxystyrene; copolymers of (meth)acrylic acid, for example with styrene; copolymers of maleiimide, for example with styrene; hydroxy or carboxy functionalised celluloses; dialkylmaleiimide esters; copolymers of maleic anhydride, for example with styrene; and partially hydrolysed polymers of maleic anhydride.

The composition is preferably such that it is patternwise solubilized by heat, during the pattern forming (exposure) process. In broad terms there are three ways in which heat can be patternwise delivered to the composition, in use. These are:-

- direct heat, by which we mean the direct delivery of heat by a heated body, by conduction. For example the composition may be contacted by a heat stylus; or the reverse face of the substrate onto which the composition has been coated may be contacted by a heated body. A heated body may be a heat stylus.

- the use of incident electromagnetic radiation to expose the composition, the electromagnetic radiation being converted to heat, either directly or by a chemical reaction undergone by a component of the composition. The electromagnetic radiation could for example be infra-red, or UV or visible radiation, depending on the composition. Preferably it is infra-red.

- the use of charged-particle radiation, for example electron beam radiation. Clearly, at the fundamental level the charged-particle mode and the electromagnetic

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1064 nm, but any laser of sufficient imaging power and whose radiation is absorbed by the composition, can be used.

5 Preferably the radiation absorbing compound is one whose absorption spectrum is such that absorption is significant at the wavelength output of the radiation source, preferably laser, which is to be used in the patternwise exposure of precursors made by the method of
10 the present invention. Usefully it may be an organic pigment or dye such as phthalocyanine pigment. Alternatively it may be a dye or pigment of the squarylium, merocyanine, cyanine, indolizine, pyrylium or metal dithioline classes.

15 In preferred compositions intended to require infrared radiation for patternwise exposure it is preferred that their developer solubility is not increased by incident UV or visible radiation, so making handling of
20 the compositions straightforward. Preferably such compositions do not comprise any UV or visible light sensitive components. However UV or visible light sensitive components which are not activated by UV or visible light due to the presence of other components,
25 such as UV or visible light absorbing dyes or a UV or visible light absorbing topmost layer, may be present in such compositions.

 Pigments are generally insoluble in the compositions
30 and so comprise particles therein. Generally they are broad band absorbers, preferably able efficiently to absorb electromagnetic radiation and convert it to heat over a range of wavelengths exceeding 200 nm, preferably exceeding 400 nm. Generally they are not decomposed by the
35 radiation. Generally they have no or insignificant effect

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In certain embodiments of the invention an additional layer comprising a radiation absorbing compound can be used. This multiple layer construction can provide routes to high sensitivity as larger quantities of absorber can be used without affecting the function of the image forming layer. In principle any radiation absorbing material which absorbs sufficiently strongly in the desired band can be incorporated or fabricated in a uniform coating. Dyes, metals and pigments (including metal oxides) may be used in the form of vapour deposited layers. Techniques for the formation and use of such films are well known in the art, for example as described in EP 0,652,483.

Said printing form precursor includes a substrate over which said heat sensitive composition is provided. Said substrate may be arranged to be non-ink-accepting. Said substrate may have a hydrophilic surface for use in conventional lithographic printing using a fountain solution or it may have a release surface suitable for use in waterless printing.

Said substrate may comprise a metal layer. Preferred metals include aluminium, zinc and titanium, with aluminium being especially preferred. Said substrate may comprise an alloy of the aforesaid metals. Other alloys that may be used include brass and steel, for example stainless steel.

Said substrate may comprise a non-metal layer. Preferred non-metal layers include layers of plastics, paper or the like. Preferred plastics include polyester, especially polyethylene terephthalate.

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resin modification, as described herein. Preferably such measures reduce the solubility of the resin, prior to the patternwise exposure. On subsequent patternwise exposure the exposed areas of the composition are rendered more soluble in the developer, than the unexposed areas. Therefore on patternwise exposure there is a change in the solubility differential of the unexposed composition and of the exposed composition. Thus in the exposed areas the composition is dissolved, to form the pattern.

The coated printing form precursor produced by the method of the invention may in use be patternwise heated indirectly by exposure to a short duration of high intensity radiation transmitted or reflected from the background areas of a graphic original located in contact with the recording material.

The developer is dependent on the nature of the polymeric substance, but is preferably an aqueous developer. Common components of aqueous developers are surfactants, chelating agents such as salts of ethylenediamine tetraacetic acid, organic solvents such as benzyl alcohol, and alkaline components such as inorganic metasilicates, organic metasilicates, hydroxides or bicarbonates.

Preferably an aqueous developer is an alkaline developer containing inorganic or organic metasilicates.

As indicated above preferred compositions to which the method of the present invention may advantageously be applied contain infra-red absorbing compounds. Examples of suitable infra-red absorbing compounds are:-

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Thus the present invention is applicable to the heat sensitive phenolic resin systems described in GB 1245924, incorporated herein by reference, these being simple systems comprising a phenolic resin and a radiation absorber, preferably a black body absorber, for example carbon black or Milori Blue, without further components to enhance the solubility differential of the composition, on patternwise exposure.

The present invention is also applicable to the systems described in US 5491046, incorporated herein by reference, whose heat sensitive compositions comprise latent Bronsted acids. These are negative working and positive working; the latter being of interest in the context of the present invention.

In the systems of US 5491046 it is said that the said heat sensitive compositions may comprise a resole resin, a novolak resin, a latent Bronsted acid and an infra-red absorber, said compositions being arranged to be sensitive to both ultraviolet and infra-red radiation.

Optionally terephthaldehyde may be included as a speed enhancing agent.

Optionally 3,4,5-trimethoxybenzoic acid may be included, to enhance image/non-image contrast.

Said resole resin may be prepared from bis-phenol A and formaldehyde. Said novolak resin may be prepared from m-cresol and formaldehyde.

The term "latent Bronsted acid" refers to a precursor which forms a Bronsted acid by decomposition. Typical examples of Bronsted acids which are suitable for this

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R⁵ and R⁶ can be an aryl group, a substituted aryl group, an aliphatic group or a substituted aliphatic group. When Y is P or As, then R⁷ can be an aryl group, a substituted aryl group, an aliphatic group or a substituted aliphatic group. W can be BF₄, CF₃SO₃, SbF₆, CCl₃CO₂, ClO₄, AsF₆, PF₆, or any corresponding acid whose pH is less than three.

Any of the onium salts described in U.S. Pat. No. 4,708,925, incorporated herein by reference, can be utilized as the latent Bronsted acid.

Use of diazonium salts as latent Bronsted acids is particularly preferred. They provide equivalent sensitivity to other latent Bronsted acids in the infrared region and higher sensitivity in the ultraviolet region.

An additional class of useful latent Bronsted acids are the haloalkyl-substituted s-triazines. The haloalkyl-substituted s-triazines are well known photolytic acid generators. Use of these compounds for this purpose is described, for example, in U.S. Pat. No 3,779,778, incorporated herein by reference.

Preferred haloalkyl-substituted s-triazines for use in this invention are compounds of the formula:



wherein R⁸ is a substituted or unsubstituted aliphatic or aromatic radical and R⁹ and R¹⁰ are, independently, haloalkyl groups.

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The present invention is also applicable to the similar systems described in US patents 5466557, 5372915 and 5372907, related to US 5491046 and likewise incorporated herein by reference.

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We also believe the present invention to be applicable to the phenolic resin systems described in US 4708925, comprising an onium salt. Suitable onium salts include iodonium, sulphonium, bromonium, chloronium, 10 oxysulphonium, sulphoxonium, selenonium, telluronium, phosphonium and arsonium salts. Preferably, an iodonium, sulphonium or oxysulphonium salt is present.

The onium salt is generally included in the 15 composition in an amount in the range from 1 to 40% by weight of the total weight of phenolic resin and onium salt. The amount of onium salt is selected to provide the desired solubility differential between the unexposed and exposed compositions. It has been found that resole 20 resins normally require the onium salt in an amount of at least 5% by weight of the total weight of phenolic resin and onium salt in order to ensure a satisfactory solubility differential. Generally, compositions employing resole resins will include at least 7% by 25 weight, of onium salt. It is possible to achieve a satisfactory solubility differential in compositions containing novolak resins containing smaller amounts of onium salt, generally in the range 1 to 40% by weight of onium salt. Suitably a further component of such 30 compositions is a spectral sensitiser in an amount of up to 10% by weight of the composition, selected from one of the following classes: diphenylmethane, xanthene, acridine, methine and polymethine, (including oxonol, cyanine and merocyanine) dye, thiazole, thiazine, azine, 35 aminoketone, porphyrin, coloured aromatic polycyclic

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"reversible insolubiliser compound", characterised in that the aqueous developer solubility of the composition is increased on heating and that the aqueous developer solubility of the composition is not increased by incident
5 UV radiation.

According to a further aspect of the '117 invention there is provided a positive working lithographic printing form precursor having a coating comprising of a
10 composition comprising a said active polymer and a said reversible insolubiliser compound coated on a support having a hydrophilic surface characterised in that the aqueous developer solubility of the composition is increased on heating and that the aqueous developer
15 solubility of the composition is not increased by incident UV radiation.

In order to increase the sensitivity of the heat-sensitive composition of the '117 invention it is
20 beneficial to include an additional component, namely a radiation absorbing compound capable of absorbing radiation and converting it to heat. Examples of suitable radiation absorbing compounds, together with the preferred amounts thereof, are given above.

25 Therefore a further aspect of the '117 invention is a lithographic printing form precursor wherein said coating is suitable adapted to preferentially absorb radiation and convert said radiation to heat.

30 Therefore according to a preferred embodiment of the '117 invention there is provided a heat-sensitive positive working lithographic printing form precursor which has on a support having a hydrophilic surface an ink-accepting
35 heat-sensitive composition comprising a said active

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employed. Thus, insubstantial increases in solubility on UV radiation may be tolerated within the scope of the '117 invention.

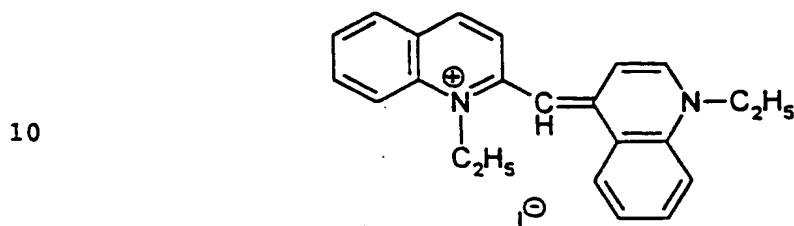
5 Thus in all preferred embodiments of the '117 invention a positive working lithographic printing form is obtained after heat-mode exposure and development. The aqueous developer solubility of the coated composition is much reduced with respect to the solubility of the active
10 polymer alone. On subsequent exposure to suitable radiation the heated areas of the composition are rendered more soluble in the developing solution, than the untreated areas. Therefore on patternwise exposure there is a change in the solubility differential of the
15 unexposed composition and of the exposed composition. Thus in the exposed areas the composition is dissolved revealing the underlying surface of the printing form.

20 Whilst the applicants do not wish to be limited by any theoretical explanation of how the '117 invention operates, it is believed that a thermally frangible complex is formed between the active polymer and the reversible insolubiliser compound. This complex is believed to be reversibly formed and can be broken by
25 application of heat to the complex to restore aqueous developer solubility to the composition. It is thought that polymeric substances suitable for use in the current invention comprise electron rich functional groups when uncomplexed and that suitable compounds which reduce the
30 aqueous developer solubility of the polymeric substance are electron poor. It is not thought that decomposition of components within the composition is required, or that any substantial decomposition has occurred in any examples tested to date.

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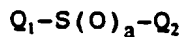
Usefully the quinolinium or benzothiazolium compounds are cationic cyanine dyes, such as Quinoldine Blue and 3-ethyl-2-[3-(3-ethyl-2(3H)-benzothiazolylidene)-2-methyl-1-propenyl] benzothiazolium iodide, and the compound of
 5 formula



15 A further useful class of reversible insolubiliser compounds are carbonyl functional group containing compounds.

20 Examples of suitable carbonyl containing compounds are α -naphthoflavone, β -naphthoflavone, 2,3-diphenyl-1-indeneone, flavone, flavanone, xanthone, benzophenone, N-(4-bromobutyl)phthalimide and phenanthrenequinone.

25 The reversible insolubiliser compound may be a compound of general formula



30 where Q_1 represents an optionally substituted phenyl or alkyl group, a represents 0, 1 or 2, and Q_2 represents a halogen atom or any alkoxy group. Preferably Q_1 represents a C_{1-4} alkyl phenyl group, for example a tolyl group, or a C_{1-4} alkyl group. Preferably a represents 1 or, especially, 2. Preferably Q_2 represents a chlorine atom or a C_{1-4} alkoxy group,
 35 group, especially an ethoxy group.

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A minor proportion as defined herein is suitably less than 50%, preferably up to 20%, most preferably up to 15%, of the total weight of the composition.

- 5 Suitably the reversible insolubiliser compound constitutes at least 1%, preferably at least 2%, preferably up to 15%, more preferably up to 25% of the total weight of the composition.
- 10 Thus a preferred weight range for the reversible insolubiliser compound may be expressed as 2-15% of the total weight of the composition.
- 15 There may be more than one active polymer which interacts with the said reversible insolubiliser compound. References herein to the proportion of such substance(s) are to their total content. Likewise there may be more than one polymeric substance which does not thus interact. References herein to the proportion of such substance(s)
- 20 are to their total content. Likewise there may be more than one reversible insolubiliser compound. References herein to the proportion of such compound(s) are to their total content.
- 25 Six simple tests, tests 1 to 6, may be carried out to determine if a composition comprising an active polymer and a reversible insolubiliser compound and a suitable aqueous developer are suitable for use as described in the '117 invention.
- 30 Test 1. The composition comprising the active polymer in the absence of the reversible insolubiliser compound is coated on a hydrophilic support and dried. Then the surface is inked-up. If a
- 35 uniform inked coating is obtained then the

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5 the reversible insolubiliser compound is heated in an oven such that the composition reaches a suitable temperature for an appropriate time. Then it is processed in a suitable aqueous developer for a reasonable period of time at room temperature.

10 The surface is then dried and inked-up. If no ink surface is obtained then the heated composition has dissolved in the developer.

15 The temperature and time depend on the components selected for the composition and on their proportion. Simple trial and error experiments may be undertaken to determine suitable conditions. If such experiments cannot yield conditions which allow the test to be passed, the conclusion must be that the composition does not pass this test.

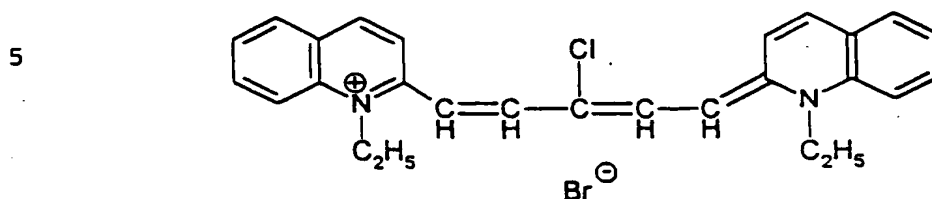
20 Preferably, for typical compositions, the composition comprising the active polymer and the reversible insolubiliser compound is heated in an oven such that the composition reaches a temperature of 50°C to 160°C for 5 to 20 seconds. Then it is processed in a suitable aqueous developer for a suitable time which may be determined by trial and error but will typically be 30 to 120 seconds, at room temperature.

30 Most preferably, the composition comprising the active polymer and the reversible insolubiliser compound is heated in an oven such that the composition reaches a temperature of 50°C to 120°C for 10 to 15 seconds. Then it is processed in a suitable aqueous developer for 30 to 90 seconds at room temperature.

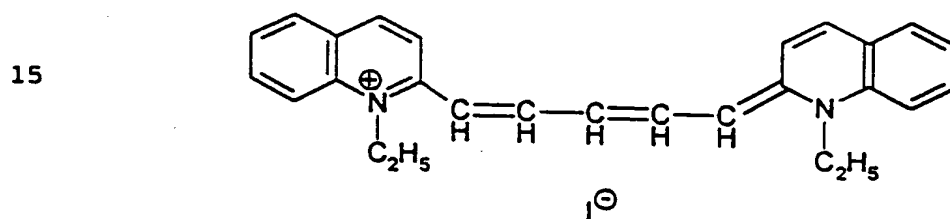
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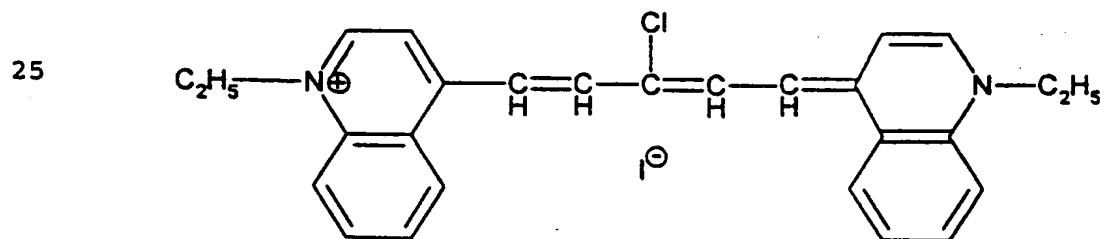
2-[3-chloro-5-(1-ethyl-2(1H)-quinolinyldiene)-1,3-pentadienyl]-1-ethylquinolinium bromide



10 1-ethyl-2-[5-(1-ethyl-2(1H)-quinolinyldiene)-1,3-pentadienyl]quinolinium iodide



20 4-[3-chloro-5-(1-ethyl-4(1H)-quinolinyldiene)-1,3-pentadienyl]-1-ethylquinolinium iodide



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such that the functionalised polymeric substance has the property that it is developer insoluble prior to delivery of radiation and developer soluble thereafter, characterised in that the functional groups Q do not
5 comprise a naphthoquinone diazide (NQD) or a benzoquinone diazide (BQD) group.

In accordance with a second aspect of the '169 invention there is provided a method for producing a
10 predetermined resist pattern on a substrate, the method comprising: the patternwise application of radiation to a precursor which comprises the substrate, having a coating thereon, the coating comprising a positive working composition; and the development of the pattern using a
15 developer; wherein the said composition comprises a polymeric substance having functional groups Q thereon, such that the functionalised polymeric substance has the property that it is developer insoluble prior to delivery of radiation and developer soluble thereafter,
20 characterised in that the functional groups Q do not contain a diazide group.

In accordance with a third aspect of the '169 invention there is provided a method for producing a
25 predetermined resist pattern on a substrate, the method comprising: the patternwise application of radiation to a precursor which comprises the substrate, having a coating thereon, the coating comprising a positive working composition; and the development of the pattern using a
30 developer; wherein the said composition comprises a polymeric substance having functional groups Q thereon, such that the functionalised polymeric substance has the property that it is developer insoluble prior to delivery of radiation and developer soluble thereafter,
35 characterised in that the functional groups are not

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additionally primarily responsible for the absorption of said radiation.

5 In relation to the '169 invention it is believed that the difference in the solubility between the functionalised polymeric substance compared with the corresponding unfunctionalised polymeric substance may involve several mechanisms but that acid generation on exposure to said radiation is not significant, in contrast
10 to existing systems. It is further believed that one important mechanism is a hydrogen bonding interaction between the functional groups Q and other groups of the polymeric substance. Intramolecular hydrogen bonding is likely to be more important but intermolecular hydrogen
15 bonding may also be important, and may even be more important in some systems. Suitably, therefore, the functionalised polymeric substance is such that there is hydrogen bonding between the said functional groups Q and other groups of the polymeric substance, in addition to
20 covalent bonding of the functional groups Q, to the polymeric substance.

In accordance with a sixth aspect of the '169 invention there is provided a method for producing a
25 predetermined resist pattern on a substrate, the method comprising: the patternwise application of radiation to a precursor which comprises the substrate, having a coating thereon, the coating comprising a positive working composition; and the development of the pattern using a
30 developer; wherein the said composition comprises a polymeric substance having functional groups Q thereon, such that the functionalised polymeric substance has the property that it is developer insoluble prior to delivery of radiation and developer soluble thereafter,
35 characterised in that there is hydrogen bonding between

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hydroxy groups thereof, but preferably not all of the hydroxy groups are thereby reacted.

5 Preferably the ratio of functional groups Q in the functionalised polymeric substance to hydroxy groups in the corresponding unfunctionalised polymeric substance is in the range 1:100 to 1:2. More preferably the said functional group ratio is in the range 1:50 to 1:3. Most preferably the said functional group ratio is in the range 10 1:20 to 1:6.

The functional groups Q suitably enable hydrogen bonding with moieties of the functionalised polymer. Suitable moieties Q known to favour hydrogen bonding and 15 which may be comprised by the functional groups Q, may include amino, monoalkylamino, dialkylamino, amido, monoalkylamido, dialkylamido, chloro, fluoro, carbonyl, sulphinyl and sulphonyl moieties.

20 Preferably the functional groups Q are bonded to the polymeric substance by an esterification reaction to form a resin ester.

A preferred composition of the '169 invention may be 25 defined by the formula $R(Q)_n$, where R is the polymer chain of the polymeric substance and (Q)_n represents functional groups bonded thereto, and Q represents a moiety which can hydrogen bond to the polymer chain R of the same molecule or an adjacent molecule or molecules. n represents a 30 plural integer.

Preferably Q represents a group of formula -T-Z where T represents a moiety which can hydrogen bond to the polymer chain R of the same molecule or an adjacent 35 molecule or molecules and Z represents a further moiety

- 43 -

- 5 - an alkyl, alkenyl or alkynyl group may be linear or branched and may contain up to 10, preferably up to 8, carbon atoms, suitable examples being methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, vinyl, allyl and propargyl. Unbranched groups may be preferred but branched groups may be employed.
- 10 - a cycloalkyl group may contain from 3 to 12, preferably 3 to 8, carbon atoms, and is suitably cyclopropyl or cyclohexyl, but could be a fused/bridged structure such as 10-camphoryl.
- 15 - the alkylene portion of an aralkyl or heteroaralkyl group is suitably a C_{1-4} alkylene group, especially methylene ($-CH_2-$).
- 20 - aryl groups are preferably naphthyl or phenyl.
- aralkyl groups are preferably (C_{1-4} alkyl)phenyl or (C_{1-4} alkyl) naphthyl, especially benzyl or naphthylmethyl.
- 25 - heteroaromatic or heterocyclic groups suitably are respectively aromatic or non-aromatic groups, containing within the carbon atom ring or rings 1 to 4 hetero atoms independently selected from oxygen, sulphur and nitrogen. Fused heteroaromatic or heterocyclic groups may be employed but preferably the group is a single ring having 5 or 6 atoms in the ring. Preferred is pyrazolyl and, especially, thienyl.
- 30 - in relation to optional substituents of the aliphatic moieties set out above, namely alkyl, cycloalkyl, alkenyl, alkynyl and heterocyclic (non-
- 35

- 45 -

aryl group is a phenyl or naphthyl group optionally substituted by 1-3 moieties independently selected from hydroxy, halo, C₁₋₄ alkyl (especially methyl), C₁₋₄ haloalkyl (especially CF₃), C₁₋₄ alkoxy (especially methoxy), amino, 5 mono-(C₁₋₄ alkyl)amino (especially methylamino), and di-(C₁₋₄ alkyl)amino (especially dimethylamino). An especially preferred aryl group is a naphthyl group, a dansyl group, a phenyl group or a 4-methylphenyl group. An especially preferred optionally substituted alkyl group is a C₂₋₈ alkyl group, especially an n-C₃₋₆ alkyl group. 10

An especially preferred composition of the invention comprises a phenolic resin, to hydroxy groups of which moieties selected from -O-SO₂-tolyl, -O-dansyl, -O-SO₂- 15 thienyl, or -O-SO₂-naphthyl and -O-CO-Ph are bonded.

It should be noted that the '169 invention is characterised in certain aspects by the presence, in the composition, of functional groups Q which do not contain 20 an NQD or BQD group. However the presence of diazide groups additional to the functional groups Q is not excluded from the above definitions of the invention.

Also, the presence, in the composition, of simple 25 diazide compounds, for example NQD or BQD compounds, is not excluded from the above definitions of the '169 invention.

Thus, one composition useful in the method of the 30 '169 invention comprises a phenolic resin having groups Q (preferably hydroxy groups to which moieties selected from -O-SO₂-tolyl, -O-dansyl, -O-SO₂-thienyl, -O-SO₂-naphthyl and -O-CO-Ph are bonded) in admixture with simple diazide-containing compounds.

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The most preferred diazide moiety when used in the practice of the '169 invention is the 1,2-naphthoquinonediazide moiety.

5 In addition to the polymeric substance, or substances, as defined above, the composition may contain an additional polymeric substance, or substances, preferably unfunctionalised phenolic resins. Such may be regarded as "inactive", in having a given level of
10 inherent developer solubility and not being functionalised to alter that inherent developer solubility, or may be regarded as an additional "active" polymeric substance, or substances, including for example an NQD resin ester. In such a composition having a blend of polymeric substances
15 it should be noted that the functionalised polymeric substance(s) of the '169 invention can be present in a lower amount, by weight, than the other polymeric substance(s). Suitably the polymeric substance of the '169 invention may be present in an amount of at least 10%,
20 preferably at least 20% by total weight of the polymeric substances present in the composition.

 It should be noted that the quantitative definitions presented above are typical ranges, and that the precise
25 selection will depend on the particular circumstances. For example the selection of highly effective functional groups Q may mean that a blend of polymeric substances may be used, with the functionalised polymeric substance(s) of the '169 invention in relatively low proportion; and/or
30 that the aforesaid functional group ratio may be lower than if a less effective functional group had been selected. The pattern-forming conditions selected and the developer to be used, will also be of relevance. The selection of a higher functional group ratio may mean that
35 a lesser amount of polymeric substance(s) of the '169

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aralkyl or heteroaralkyl group, each such group being optionally substituted; wherein optional substituents of the aryl and heteroaryl groups, and of the aryl and heteroaryl parts of the aralkyl or heteroaralkyl groups, are selected from halo, nitro, cyano, hydroxy, thiol, amino, optionally substituted mono-C₁₋₄ alkylamino, optionally substituted di-C₁₋₄ alkylamino, amido, optionally substituted mono-(C₁₋₄ alkyl)amido, optionally substituted di-(C₁₋₄ alkyl)amido, optionally substituted C₂₋₄ alkenyl, optionally substituted C₁₋₄ alkyl, optionally substituted C₁₋₄ alkoxy, (C₁₋₄ alkyl)carbonylamino, -COOH, optionally substituted (C₁₋₄ alkyl)carbonyl and optionally substituted (C₁₋₄ alkoxy)carbonyl groups; and wherein optional substituents of the alkyl, alkenyl, alkynyl, cycloalkyl and non-aromatic heterocyclic groups, and of the alkyl parts of the aralkyl and heteroaralkyl groups, and of the alkyl, alkoxy, alkylamino, alkylamido, alkylcarbonyl, alkoxycarbonyl, alkylcarbonylamino and alkenyl moieties optionally substituting said aryl or heteroaryl moieties are selected from halo, nitro, cyano, carbonyl, hydroxy, thiol, amino, mono-C₁₋₄ alkylamino, di-C₁₋₄ alkylamino, amido, mono-(C₁₋₄ alkyl)amido, di-(C₁₋₄ alkyl) amido, C₁₋₄ alkoxy, -COOH, (C₁₋₄ alkyl)carbonylamino, (C₁₋₄ alkyl)carbonyl and (C₁₋₄ alkoxy)carbonyl groups.

Simple tests may be carried out to determine if the phenolic resin composition is likely to be suitable for use in the '169 invention. Such tests may be substantially as described above in relation to the '117 invention, except that they are applied to the "unfunctionalised polymeric substance" and "functionalised polymeric substance" of the '169 invention, rather than the "active polymer" and "active polymer and reversible insolubiliser compound" of the '117 invention; and except that Test 6 described above in relation to the '117

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substance in the presence of said diazide moieties. Preferably, in practical terms it may be regarded as a soluble polymeric substance.

5 In order to increase the sensitivity of the heat-sensitive composition of the '172 invention it is beneficial to include an additional component, namely a radiation absorbing compound capable of absorbing radiation and converting it to heat. Examples of suitable
10 radiation absorbing compositions, together with the preferred amounts thereof, are given above.

Diazide moieties used in the '172 invention preferably comprise diazo groups $=N_2$ conjugated to carbonyl
15 groups, preferably via an aromatic or heteroaromatic ring. In such moieties a carbonyl group is preferably bonded to the aromatic or heteroaromatic ring at an adjacent ring position to the diazo group. Preferred moieties are o-benzoquinonediazide (BQD) moieties (often referred to as
20 o-quinonediazides) and o-naphthoquinonediazide (NQD) moieties.

A BQD moiety may, for example, comprise the 1,4- or, preferably 1,2-benzoquinonediazide moiety.
25

An NQD moiety may, for example, comprise the 1,4-, 2,1- or, most preferably, the 1,2-naphthoquinone diazide moiety.

30 Generally, NQD moieties are preferred to BQD moieties in the practice of the '172 invention.

Most preferred in the practice of the '172 invention is the 1,2-naphthoquinonediazide moiety.
35

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The diazide moieties may be present as simple compounds admixed with the polymeric substance or, as is preferred, as moieties covalently bonded to the polymeric substance. It should be noted that moieties not comprising diazide moieties, may additionally be covalently bonded to the polymeric substance; or may advantageously be functional groups of an additional polymeric substance, within the composition. Such moieties are suitably moieties Q of the '169 invention, as previously described; the earlier definitions thereof apply here.

The method of the '172 invention as set out above is a positive working method but it has also been determined that by means of a further step a negative working method is possible. This requires an overall exposure to UV radiation subsequent to the said patternwise application of radiation, and prior to the said application to the coating of the developer. It is then found that the areas of the coating not exposed to the patternwise radiation dissolve. This constitutes a further aspect of the '172 invention. The heat treatment method of the present invention may advantageously be applied to precursors intended for this mode of exposure.

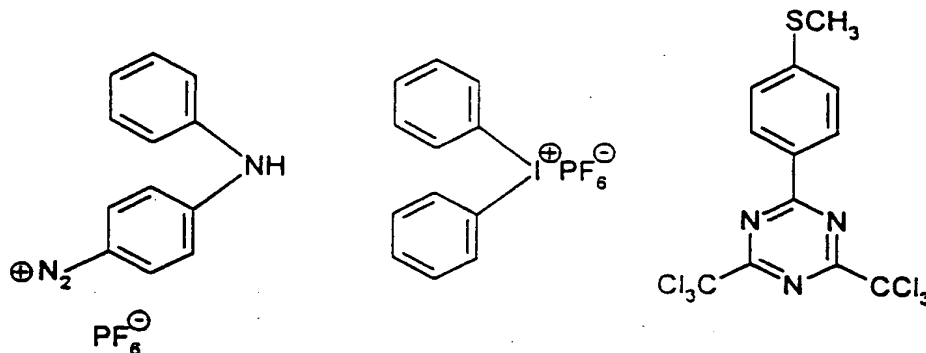
Simple tests may be carried out to determine if the composition comprising the polymeric substance, the selected developer and hydrophilic support, are together likely to be suitable for the positive working method of the '172 invention. The tests are as described earlier with reference to the '117 invention except that they are applied to the "polymeric substance" and "polymeric substance and diazide moieties" of the '172 invention rather than the "active polymer" and "reversible insolubiliser compound" of the '117 invention; and except that Test 6 thereof is not likely to be required.

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A preferred bis-hydroxyalkyl compound is a bis-hydroxymethyl compound, with 2,6-bis(hydroxymethyl)-p-cresol being especially preferred.

Said latent acid generating compound may be a latent Bronsted acid for example as described above in relation to the other compositions to which the invention can be applied.

Preferred latent acid generating compounds are:



That concludes the general description of our earlier '877 invention, to which the present invention can be applied.

The methods of the present invention as defined above may be applied to our novel compositions as described in our unpublished patent application GB 9722862.1 (hereinafter "the '862 invention"). The pages which follow are incorporated from that specification. The term "heat sensitive composition" as used in the description which follows denotes the composition comprising the phenolic resin, of the present invention.

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Unless otherwise stated in relation to the developer resistance means, an alkyl group may have up to 12, suitably up to 10, preferably up to 8, more preferably up to 6, especially up to 4 carbon atoms.

5

Unless otherwise stated in relation to the developer resistance means, where any group is stated to be "optionally-substituted", it may be substituted by one or more: halogen atoms, especially fluorine, chlorine or bromine atoms; hydroxy or cyano groups; carboxyl groups or carboxy derivatives, for example carboxylic acid salts; and optionally-substituted alkyl, alkenyl, alkynyl, alkoxy, amino, sulphinyl, sulphonyl, sulphonate and carbonyl groups.

15

Compounds in group (A) may include a unit of formula
$$[-C_rH_{2r}-O-]_y$$
 I wherein r is an integer in the range 2 to 5 and y is an integer in the range 2 to 5,000. The moiety $-C_rH_{2r}-$ may include straight or branched chains.

20

Preferably, r represents 2 or 3. Where r represents 3, said unit of formula I may represent a 1- or, preferably, a 2-oxypropylene unit.

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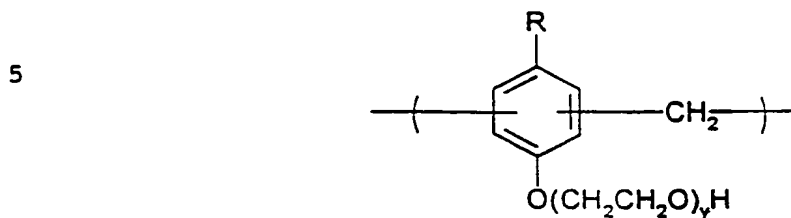
Suitably, y is less than 500, is preferably less than 350, is more preferably less than 200 and, especially, is less than 100.

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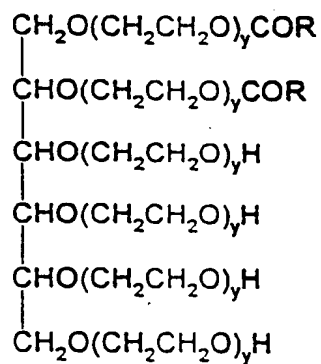
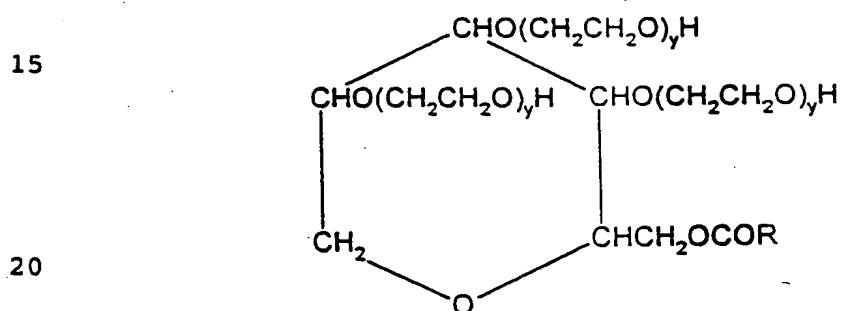
Examples of compounds in group (A) include the following, wherein R represents a hydrogen atom or an optionally-substituted, preferably an unsubstituted, alkyl or phenyl group; l represents 0 to 3, preferably 1; z is suitably less than 500, is preferably less than 350, is

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ethylene oxide derivatives of alkylphenol-formaldehyde condensate



10 polyoxyethylene-polyhydric alcohol fatty acid partial esters such as



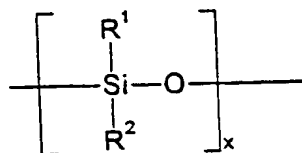
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lauryl ether, polyoxyethylene cetyl ether, polyoxyethylene
 stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene
 higher alcohol ether, polyoxyethylene octylphenyl ether,
 polyoxyethylene nonylphenyl ether,
 5 polyoxyethylene sorbitan monolaurate, polyoxyethylene
 sorbitan monopalmitate, polyoxyethylene sorbitan
 monostearate, polyoxyethylene sorbitan tristearate,
 polyoxyethylene sorbitan monooleate, polyoxyethylene
 sorbitan trioleate, polyoxyethylene sorbitol tetraoleate,
 10 polyethylene glycol monooleate, polyethylene glycol
 distearate, polyoxyethylene nonylphenyl ether-formaldehyde
 condensate, oxyethylene-oxypropylene block copolymer,
 polyethylene glycol, tetraethylene glycol, polyoxyethylene
 stearyl ether, polyoxyethylene sorbitol lauryl ester, and
 15 polyoxyethylene castor oil.

Compounds in group (B) include siloxanes substituted
 by one or more optionally-substituted alkyl or phenyl
 groups. Said siloxane may be linear, cyclic or complex
 20 cross-linked. Preferred siloxanes are phenylalkylsiloxanes
 and dialkylsiloxanes.

Preferred compounds in group (B) include a unit of
 formula

25



30

wherein R¹ and R² independently represent an optionally-
 substituted, especially an unsubstituted, alkyl or phenyl
 group and x represents an integer.

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lauryl, cetyl, stearyl, oleyl and phenyl ethers. Preferred amides are fatty acid alkanolamides, with lauryl ethanolamide being especially preferred.

5 Compounds in group (C) may comprise any of the compounds described above for group A, but excluding the polyalkylene oxide unit of such compounds.

10 Said heat sensitive composition and said developer resistance means of said precursor may not necessarily, together, define a single homogenous layer. Said precursor may include at least some developer resistance means at or towards an upper surface thereof.

15 Whilst the applicants do not wish to be limited by any theoretical explanation of how the '862 invention operates, it is believed that the presence of at least part of the developer resistance means at an uppermost surface of the precursor may be a key factor. Thus,
20 preferably, the precursor includes an upper surface (which is suitably contacted by developer during development) which includes some of said developer resistance means. Such a surface may be a component of a layer which also includes said heat sensitive composition. In this case,
25 the precursor may be prepared using a mixture comprising said heat sensitive composition and said developer resistance means. It is believed that, at some stage, at least part of the developer resistance means separates from the heat sensitive composition and migrates to the
30 surface. Thus, resistance to developer attack appears to be manifested particularly at the surface of precursors of the present invention. Dynamic contact angle studies (using a Cahn Dynamic Contact Angle Analyzer) have clearly showed a marked effect at the surface of precursors
35 described herein. For example, a typical positive working

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According to a second aspect of the '862 invention, there is provided a precursor for preparing a resist pattern by heat mode imaging, the precursor comprising:

5 a heat sensitive composition, the solubility of which in an aqueous developer is arranged to increase in heated areas, where in said composition comprises an aqueous developer soluble polymeric substance (referred to above as the "active polymer") and a compound which reduces the
10 aqueous developer solubility of the polymeric substance (referred to above as the "reversible insolubiliser compound"); and

a surfactant;

15 wherein the aqueous developer solubility of the composition is increased on heating and the aqueous developer solubility of the composition is not increased by incident UV radiation.

20 The "heat sensitive composition" of the '862 invention may be any of the various heat sensitive compositions defined hereinabove, to which the present invention can be applied. This '862 invention involves
25 the inclusion of a said developer resistance means, as a component of any of the aforementioned heat mode compositions. The simple test methods described above in relation to those inventions may be used to determine the likely suitability of a composition of the '862 invention,
30 as a printing form coating.

That concludes the general description of our co-filed invention entitled "Pattern Formation" to which the present invention can be applied.

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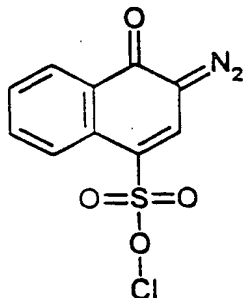
Resin C: LB6564 phenolic resin modified by simple reaction with p-toluene sulphonyl chloride as follows.

- 5 1. Dissolve LB 6564 (25.0 g) resin (Resin A) in 61.8 g of 2-methoxyethanol.
2. Immerse a three-necked 500 ml round-bottomed flask in a water bath placed on a hot plate/stirrer. Attach a stirrer gland, stirring rod and a thermometer to the flask.
- 10 3. Place the resin solution into the flask and begin rapid stirring.
4. Slowly add 25.6 g of distilled water drop-wise keeping precipitation to a minimum.
- 15 5. Add sodium hydrogen carbonate (4.3 g) to the flask. Not all of the solid will dissolve.
6. Slowly add the acid chloride (1.18 g) with vigorous stirring.
7. Warm the reaction mixture for 6 hours at 40°C with stirring.
- 20 8. After 6 hours, remove the flask from the water bath and allow to cool (about 30 mins).
9. Prepare a dilute solution by adding 8.6 g of 1.18 s.g. hydrochloric acid to 354 g of distilled water.
- 25 10. Slowly precipitate the esterified resin drop-wise into the dilute acid with stirring.
11. Filter and wash the precipitate by re-slurrying in distilled water at least three times if possible until the pH of the filtrate reaches 6.0.
- 30 12. Dry the precipitate in a vacuum oven at 40°C. 75% yield. Identity confirmed by IR spectroscopy.

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6. Slowly add the acid chloride (4.5 g) with vigorous stirring.
7. Warm the reaction mixture for 6 hours at 40°C with stirring.
- 5 8. After 6 hours, remove the flask from the water bath and allow to cool (about 30 mins).
9. Prepare a dilute solution by adding 8.6 g of 1.18 s.g. hydrochloric acid to 354 g of distilled water.
- 10 10. Slowly precipitate the esterified resin drop-wise into the dilute acid with stirring.
11. Filter and wash the precipitate by re-slurrying in distilled water at least three times if possible until the pH of the filtrate reaches 6.0.
12. Dry the precipitate in a vacuum oven at 40°C. 75%
15 yield. Identity confirmed by IR spectroscopy.

(214-NQD chloride - the compound

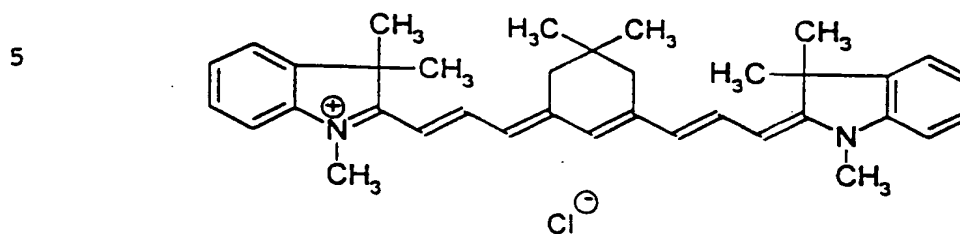


supplied by A.H. Marks, Bradford, UK).

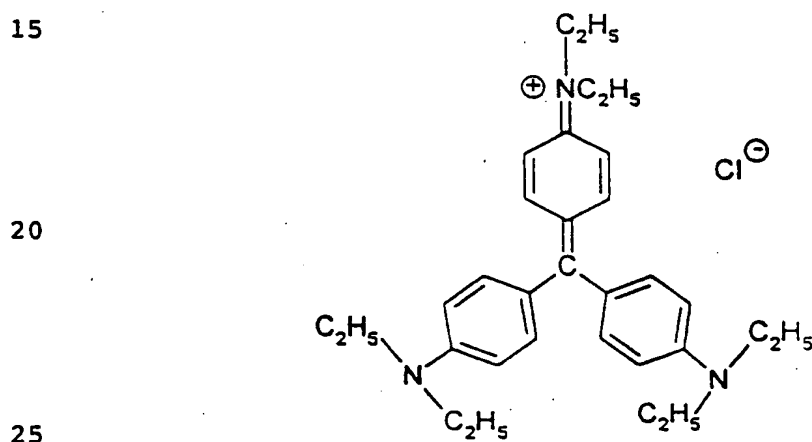
- 30 Resin H: Durite PD-494A, a cresylic resin supplied by Borden, Columbus, Ohio, USA.

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Dye C - I-1-62L as supplied by H.W. Sands of Jupiter, Florida, USA, believed to have the structure:



Dye D - Ethyl violet (Basic Violet 4, C.I. 42600) as supplied by Aldrich Chemical Company, Dorset, UK, having the structure:



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Silikophen P50X - a phenyl methyl siloxane as supplied by Tego Chemie Service GmbH of Essen, Germany.

5 Carbon black FW2 - a channel type carbon black as supplied by Degussa, of Macclesfield, UK.

Prussian blue - ferric ferrocyanide, CI pigment Blue 27, supplied by Aldrich.

10 Developer A - 14% wt sodium metasilicate pentahydrate in water.

Developer B - 7% wt sodium metasilicate pentahydrate in water.

15 Substrate A - 0.3 mm sheet aluminium electrograined and anodised and post-anodically treated with an aqueous solution of an inorganic phosphate.

Exposure Test Methods

20

Printing plate precursors made according to the Examples 1 to 11 below were imaged in a commercially available image setter, the Trendsetter 3244 using Procomm Plus software, operating at a wavelength of 830 nm at powers of up to 8 W and supplied by Creo Products Inc. of Burnaby, Canada.

30 For Examples 12 to 14 below the coated substrate to be imaged was cut into a circle of 105 mm diameter and placed on a disc that could be rotated at a constant speed of 2500 revolutions per minute. Adjacent to the spinning disc a translating table held the source of the laser beam so that the laser beam impinged perpendicularly onto the coated substrate, while the translating table moved the
35 laser beam radially in a linear fashion with respect to

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Individual plate samples were then covered with interleaving (a polythene coated paper No. 22, 6 gm² as supplied by Samuel Grant, U.K.), wrapped in paper (unbleached, unglazed Kraft 90 gm², coated with matt black low density polythene 20 gm² as supplied by Samuel Grant, U.K.) and placed in an Gallenkamp hotbox oven with fan, size 2, as supplied by Sanyo Gallenkamp plc of Leicester, U.K., at 50°C for 0, 2, 3, 5 and 12 days respectively.

The resulting heat treated plates were imaged using the Creo Trendsetter at 7 watts with a 50% screen image at imaging energy densities of 120, 140, 160, 180, 200 and 220 mJcm². The plates were developed using a Horsell Mercury Mark V plate processor containing developer A at 22°C. The processing speed was set at 1000 mm min⁻¹. Finally, images produced were evaluated visually and the energy required to produce a 50% imaged plate was recorded (mJcm²).

20

	Number of days plates having resided in oven at 50°C				
	0	2	3	5	12
Energy required to produce 50% image/mJcm ²	No coating retained	140-160	160-180	160-180	160-180

25

Example 2

A coating formulation for example 2 as described below, was prepared as a solution in 1-methoxypropan-2-ol/xylene 98:2 (w:w). The formulation was coated as described in example 1 onto Substrate A to provide the specified dry film composition with a coating weight of 2.0 gm², after thorough drying at 130°C for 80 seconds in a Mathis labdryer oven.

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Ivyland, Pennsylvania, U.S.A. and are expressed in the following table.

Densitometer readings for example 2

	Time of heat treatment (hours)																
	0.03	0.07	0.1	0.13	0.17	0.2	0.3	0.5	0.8	1	2	5	10	20	24	28	48
50°C										45%				48%		57%	54%
85°C							43%	46%		47%	50%				52%		55%
110°C							36%	42%	43%						80%		85%
140°C	36%	52%	65%	70%	71%	78%						100%	100%				

Example 3

The coating formulation of example 1 was prepared as a solution in 1-methoxypropan-2-ol/xylene 98:2 (w:w). The formulation was reverse roller coated onto Substrate A. The solution concentration was selected to provide the specified dry film composition with a coating weight of 2.5 gm², after thorough drying at 140°C for 30 seconds in an air flotation oven.

10

Plates were individually wrapped in paper (unbleached, unglazed Kraft 90 gm², coating with matt black low density polythene 20 gm²) and placed in a Gallenkamp hotbox oven with fan, size 2 at 50°C for 0, 17, 24 and 70 hours. The resulting heat treated plates were then imaged at 8 watts with a 50% screen image using the Creo Trendsetter as described previously at an imaging energy density of 180 mJcm². The plates were developed using a

15

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Mercury Mark V plate processor containing developer A at 22°C. The processing speed was set at 1000 mm min⁻¹.

Finally, images produced were evaluated visually and the energy required to produce a 50% image was recorded as 180 mJcm⁻².

Examples 5-8

Coating formulations set out below were prepared as a solution in 1-methoxypropan-2-ol/xylene 98:2 (w:w). The formulations were coated as described in example 1 onto Substrate A to provide the specified dry film composition with a coating weight of 2.0 gm² after thorough drying at 100°C for 3 minutes in a Mathis labdryer oven.

	Ex. 5	Ex. 6	Ex. 7	Ex. 8
Resin A	93.5	92.5	91	92
Monazoline C	1	1	2.5	0
Dye C	2	3	3	4
Dye D	0.5	0.5	0.5	1
Silikophen P50X	3	3	3	3

25

Plates were individually covered with interleaving (a polythene coated paper 6 gm⁻²), wrapped in paper (unbleached, unglazed Kraft 90 gm⁻², coated with matt black low density polythene 20 gm⁻²) and placed in a Gallenkamp hotbox oven with fan, size 2 under the following conditions:

30

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film composition with a coating weight of 2.0 gm^2 after thorough drying at 130°C for 80 seconds in a Mathis labdryer oven.

5 Plate samples were then either:

1. covered with interleaving (a polythene coated paper, 6 gm^2), and then wrapped as a 13 plate packet in paper (unbleached, unglazed Kraft 90 gm^2 , coated with matt black low density polythene 20 gm^2)

or 2. left un-interleaved but wrapped as a 13 plate packet in paper (unbleached, unglazed Kraft 90 gm^2 , coated with matt black low density polythene 20 gm^2)

and placed in a Gallenkamp hotbox oven with fan, size 2, for various times (0 to 80 hours) at 50°C . The resulting heat treated plates were then imaged with 50% screen images using the Creo Trendsetter as described previously at an imaging energy density of 200 mJcm^2 . The plates were developed using a Horsell Mercury Mark V plate processor containing developer A at 22°C . The processing speed was set at 700 mm min^{-1} . Finally, images produced were read using the Tobias plate check densitometer. The results are expressed in the table below.

Densitometer readings for example 9

	Time of heat treatment (hours)													
	4	6	9	18	24	28	32	45	48	50	52	57	60	75
not interleaved	20%	32%		47%	47%	47%		49%					50%	50%
interleaved		34%	42%		48%		50%		50%	50%	50%	51%		51%

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Results for plates heat treated at 40°C

		Number of days plates have resided in oven				
		0	4	6	8	10
Processing Speed mm min ⁻¹	500	0%	51%	52%	64%	65%
	1500	0%	71%	73%	72%	67%

Results for plates heat treated at 50°C

		Number of days plates have resided in oven				
		0	1	2	3	10
Processing Speed mm min ⁻¹	500	0%	53%	47%	47%	68%
	1500	0%	72%	70%	67%	83%

Results for plates treated at room temperature

		Number of days plates have resided in oven			
		0	5	12	17
Processing Speed mm min ⁻¹	500	0%	10%	22%	41%
	1500	0%	18%	47%	60%

It should be noted that example 10 gives the results of preliminary tests on the compositions containing Resin C and the heat treatment conditions were far from optimised. However we believe the results show that a temperature above room temperature will be required to get good stability, and that heat treatment at a temperature

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plate processor containing developer A at 22°C. The processing speed was set at 750 mm min⁻¹. Finally, images produced were evaluated visually and the energy required to produce a 50% image was recorded.

5

	Imaging Energy Density/mJcm ⁻²															
	150				200				250				300			
Age of plate/days	0	1	2	4	0	1	2	4	0	1	2	4	0	1	2	4
Plates placed in oven	5%	33%	35%	47%	0%	27%	30%	44%	0%	26%	32%	40%	0%	14%	39%	40%
Plates stored at room temp.	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%

Examples 12 to 14

Coating formulations were prepared as described in example 1 as solutions in 1-methoxypropan-2-ol/dimethylformamide 50:50 (w:w) for examples 12 and 13 and as solutions in 1-methoxypropan-2-ol for Example 14. The formulations were coated as previously described onto Substrate A to provide the specified dry film composition with coating weights of 1.2 gm² for examples 12 and 13, and a coating weight of 2.5 gm² for example 14, after thorough drying at 130°C for 80 seconds in a Mathis labdryer oven.

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In addition, plate samples of example 12 were tested for developability by immersing in developer B at 20°C for an appropriate time and plate samples of examples 13 and 14 were tested for developability by immersing in developer A at 35°C for an appropriate time. The second column in the following table lists the results of these simple developability tests for the compositions.

		Immersion time required/seconds	Time to fully remove coating/seconds
Example 12	Samples placed in oven	60	35
	Samples stored at room temperature	30	3
Example 13	Samples placed in oven	120	120
	Samples stored at room temperature	60	90
Example 14	Samples placed in oven	40	45
	Samples stored at room temperature	30	15

For example 15 Prussian Blue and resin B (at a ratio of 1:4, w:w) were ball milled together for four days such that the dispersed mill-base had a solids content of 30% in 1-methoxy-2-propyl acetate and a particle size of <10 microns as determined by grind gauge.

For example 16, Prussian blue and resin H were ball milled as described above.

For example 17, Carbon black FW2 and resin B were ball milled as described above.

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Plate samples were then imaged on the Trendsetter 3244, using the internal test pattern, plot 0 (50% screen) at 10W, 200 mJcm⁻², 127 rpm.

The exposed samples were then processed by immersing in developer B at 21°C for an appropriate time as described below. Other samples were processed using a Horsell Mercury Mark V processor filled with Developer A at 22.5°C and having a plate speed of 1500 mm/min. The images (written as 50% dots) were measured using a Tobias plate check densitometer as supplied by Tobias Associates Inc, of Ivyland, Pennsylvania, USA.

	Processing by Immersion		Processing using Mercury Mark V
	Time/seconds	Written 50% dots	Written 50% dots
Example			
15	15	52%	47%
16	30	46%	67%
17	15	47%	52%

In the specification we refer in various places to UV, infra-red and visible radiation. A person skilled in the art will be aware of the typical wavelength ranges of these radiations. However, for the avoidance of any doubt, UV radiation typically has a wavelength range not exceeding about 450 nm (by which we mean insubstantial above 450 nm). Visible radiation has a wavelength range of about 400 to 700 nm. Infra-red radiation typically has a wavelength range in excess of 600 nm, the boundaries between UV and visible radiation, and between infra-red and visible radiation, not being sharp ones.

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CLAIMS

1. A method of manufacturing a printing form precursor which comprises a coating on a substrate, the coating comprising a positive working composition which comprises a phenolic resin, wherein the method of manufacturing comprises the application of the composition in a solvent to the substrate, the drying of the composition, and the subsequent heat treatment of the coated substrate.
2. A method as claimed in Claim 1, wherein the heat treatment is carried out at a temperature in the range 40-90°C.
3. A method as claimed in Claim 2, wherein the heat treatment is carried out in the range 45-85°C.
4. A method as claimed in Claim 3, wherein the heat treatment is carried out in the range 50-60°C.
5. A method as claimed in any preceding claim, wherein the heat treatment is carried out for at least 4 hours.
6. A method as claimed in any preceding claim, wherein the heat treatment is carried out for at least 24 hours.
7. A method as claimed in any preceding claim, wherein the drying of the composition is carried out by subjecting the substrate carrying the composition in a solvent to a temperature exceeding the temperature selected for the heat treatment, and for a period of time less than that selected for the heat treatment.

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15. A method as claimed in Claim 14 wherein the composition is such that the radiation to which it is sensitive is of wavelength entirely or predominantly exceeding 500 nm.
16. A method as claimed in Claim 15, wherein the composition is such that the radiation to which it is sensitive is electromagnetic radiation entirely or predominantly in the range 600 to 1400 nm.
17. A method as claimed in any of Claims 13 to 16, wherein the composition is such that it may be patternwise exposed by radiation delivered by a laser.
18. A method as claimed in any of Claims 13 to 17, wherein the coating is such that on patternwise exposure to radiation it converts said radiation to heat.
19. A method as claimed in any of Claims 13 to 17, wherein the composition is such that on imagewise exposure to radiation said composition itself absorbs said radiation and converts said radiation to heat.
20. A method as claimed in Claim 19, wherein said composition comprises a radiation absorbing compound able to absorb said radiation and convert it to heat.
21. A method as claimed in Claim 18, wherein said coating comprises an additional layer disposed beneath the said composition, wherein the additional layer comprises a radiation absorbing compound able to absorb said radiation and convert it to heat.

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31. A method as claimed in any preceding claim, wherein the composition comprises an aqueous developer soluble phenolic resin and a compound which reduces the aqueous developer solubility of the phenolic resin characterised in that the aqueous developer solubility of the composition is increased on heating and that the aqueous developer solubility of the composition is not increased by incident UV radiation.
32. A method as claimed in Claim 31, wherein said compound which reduces the aqueous developer solubility of the phenolic resin is a compound which comprises at least one nitrogen atom which is quarternised.
33. A method as claimed in Claim 31, wherein the compound which reduces the aqueous developer solubility of the phenolic resin is a compound which comprises at least one nitrogen atom incorporated in a heterocyclic ring.
34. A method as claimed in claim 33, wherein the compound which reduces the aqueous developer solubility of the phenolic resin is selected from a quinoline and a triazole.
35. A method as claimed in Claim 31, wherein the compound which reduces the aqueous developer solubility of the phenolic resin is a compound which comprises at least one quarternised nitrogen atom incorporated in a heterocyclic ring.
36. A method as claimed in Claim 35, wherein the compound which reduces the aqueous developer solubility of the

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Where Q_1 represents an optionally substituted phenyl or alkyl group, n represents 0, 1 or 2, and Q_2 represents a halogen atom or an alkoxy group.

44. A method as claimed in Claim 31, wherein the compound which reduces the aqueous developer solubility of the phenolic resin is selected from ethyl-p-toluene sulphonate and p-toluenesulphonyl chloride.
45. A method as claimed in Claim 31, wherein the compound which reduces the aqueous developer solubility of the phenolic resin is acridine orange base (CI solvent orange 15).
46. A method as claimed in Claim 31, wherein the compound which reduces the aqueous developer solubility of the phenolic resin is a ferrocenium compound.
47. A method as claimed in Claim 20 and in Claim 31, wherein the compound which reduces the aqueous developer solubility of the phenolic resin is also a radiation absorbing compound able to absorb said radiation and convert it to heat.
48. A method as claimed in Claim 47, wherein the compound which reduces the aqueous developer solubility of the phenolic resin and is also a radiation absorbing compound is a cyanine dye which comprises a quinolinium moiety.
49. A method as claimed in any of Claims 1 to 30, wherein the phenolic resin has functional groups Q thereon, such that the functionalised phenolic resin has the property that it is developer insoluble prior to delivery of radiation and developer soluble

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thereafter, wherein the functional groups Q are not additionally primarily responsible for the absorption of said radiation.

54. A method as claimed in any of Claims 1 to 30, wherein the phenolic resin has functional groups Q thereon, such that the functionalised phenolic resin has the property that it is developer insoluble prior to delivery of radiation and developer soluble thereafter, wherein there is hydrogen bonding between said functional groups Q and other groups of the same molecule or other molecule(s) of the polymeric substance.
55. A method as claimed in any of Claims 49 to 54, wherein the functional groups Q are selected from groups which comprise amino, monoalkylamino, dialkylamino, amido, monoalkylamido, dialkylamido, chloro, fluoro, carbonyl, sulphinyl or sulphonyl moieties.
56. A method as claimed in any of Claims 49 to 55, wherein the functionalised phenolic resin is defined by the formula $R-(Q)_n$, wherein R represents the polymer chain of the phenolic resin and $(Q)_n$ represents functional groups bonded thereto, wherein Q represents a group of formula -T-Z where T represents a moiety which hydrogen bonds to the polymer chain R of the same molecule or an adjacent molecule or molecules and Z represents a further moiety which optionally hydrogen bonds to the polymer chain R of the same molecule or an adjacent molecule or molecules.

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general formula $R(Q)_n$, where R is the polymer chain of the phenolic resin, and Q represents a group of formula $-O-T'-Z$ where T' represents a carbonyl group, a sulphinyl group or a sulphonyl group, or a group of the formula $-O-X(Z)-O-$ where X represents a group $-P(O)-$; wherein Z represents an alkyl, alkenyl, alkynyl, cycloalkyl, aryl, heteroaryl, non-aromatic heterocyclic, aralkyl or heteroaralkyl group, each such group being optionally substituted; wherein optional substituents of the aryl and heteroaryl groups, and of the aryl and heteroaryl parts of the aralkyl or heteroaralkyl groups, are selected from halo, nitro, cyano, hydroxy, thiol, amino, optionally substituted mono- C_{1-4} alkylamino, optionally substituted di- C_{1-4} alkylamino, amido, optionally substituted mono- $(C_{1-4}$ alkyl)amido, optionally substituted di- $(C_{1-4}$ alkyl)amido, optionally substituted C_{2-4} alkenyl, optionally substituted C_{1-4} alkyl, optionally substituted C_{1-4} alkoxy, $(C_{1-4}$ alkyl)carbonylamino, $-COOH$, optionally substituted $(C_{1-4}$ alkyl)carbonyl and optionally substituted $(C_{1-4}$ alkoxy)carbonyl groups; and wherein optional substituents of the alkyl, alkenyl, alkynyl, cycloalkyl and non-aromatic heterocyclic groups, and of the alkyl parts of the aralkyl and heteroaralkyl groups, and of the alkyl, alkoxy, alkylamino, alkylamido, alkylcarbonyl, alkoxycarbonyl, alkylcarbonylamino and alkenyl moieties optionally substituting said aryl or heteroaryl moieties are selected from halo, nitro, cyano, carbonyl, hydroxy, thiol, amino, mono- C_{1-4} alkylamino, di- C_{1-4} alkylamino, amido, mono- $(C_{1-4}$ alkyl)amido, di- $(C_{1-4}$ alkyl) amido, C_{1-4} alkoxy, $-COOH$, $(C_{1-4}$ alkyl)carbonylamino, $(C_{1-4}$ alkyl)carbonyl and $(C_{1-4}$ alkoxy)carbonyl groups.

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said developer resistor means comprises one or more compounds selected from the groups comprising:

- (A) compounds which include a poly(alkylene oxide) unit;
 - (B) siloxanes; and
 - (C) esters, ethers and amides of polyhydric alcohols.
72. A method as claimed in any of claims 1 to 10, wherein the composition comprises a phenolic resin and diazide moieties.
73. A positive working lithographic printing form precursor per se produced by a method as claimed in any preceding claim.
74. A method of producing a printing form, comprising an exposure step of effecting heating of selected areas of the composition of a precursor as claimed in Claim 73, such as to render such areas developer soluble, followed by development in an aqueous developer to remove said selected areas.
75. A lithographic printing form produced by a method as claimed in Claim 74.
76. A method of manufacturing a printing form precursor, or a printing form precursor per se, or a method of producing a printing form or a printing form per se, each being independently substantially as hereinbefore described with reference to the Examples.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 98/03191

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,A	WO 97 39894 A (HOARE RICHARD DAVID ;HORSELL GRAPHIC IND LTD (GB); PARSONS GARETH) 30 October 1997 cited in the application -----	1-76